Wettability of Solid Surface. V. The Effect of Metallic Cations on Wettability of Stearic Acid⁽¹⁾

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Introduction

In one of the preceding reports,⁽²⁾ it was pointed out that the wettability of stearic acid surface was increased by treating with aluminum or thorium salt solution, while it was not increased by treating with potassium or calcium salt solution. Langmuir also showed that the wettability of barium stearate built-up film was increased by treating with aluminum or thorium salt solution,⁽³⁾⁽⁴⁾ and further that some properties of stearic acid monolayer were changed by adsorption of these metallic ions.⁽⁵⁾ However, the present author has found no explanation for the mechanism of wetting due to ions like aluminum and thorium. The present paper describes the effect of various metallic ions on the wettability of stearic acid as well as the explanation of its mechanism.

Experimental

Material.—Stearic acid of Kahlbaum was used after recrystallization from alcohol. Salts used were LiCl, NaCl, RbCl, $MgSO_4 \cdot 7H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $BaCl_2 \cdot 2H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $CuSO_4 \cdot 5H_2O$, $AgNO_3$, $ZnSO_4 \cdot 7H_2O$, $3CdSO_4 \cdot 8H_2O$, $HgCl_2$, $Pb(NO_3)_2$, $Th(NO_3)_4$, $MnSO_4 \cdot 6H_2O$, $FeK(SO_4)_2 \cdot 12H_2O$, $Co(NO_3)_2$, and $NiSO_4 \cdot 7H_2O$. These salts were recrystallized from redistilled water before use. Special purification was made prior to the recrystallization if necessary. Water used for the wettability experiment was also redistilled using the apparatus of Vidrex glass of Kokura Glass Co. and was made free from carbon dioxide.

Measurement.—A clean glass rod of about 5 mm. diameter and 50 mm. length was dipped into molten stearic acid, withdrawn, and thus coated with a layer of stearic acid which was solidified in air. The surface of stearic acid thus obtained was treated with various salt solutions for about seventeen hours, after which the wettability of the surface was measured in relation to the same solution. The concentration of the solution used was kept to 10^{-4} mol unless mentioned otherwise. pH of the solution was controlled simply using hydrochloric acid or sodium hydroxide solution.

For wettability measurement, the sessile drop method was used. Namely, a drop of 0.5 mm. diameter was placed on the surface for measurement with the aid of a glass capillary having a paraffined tip. The image of the drop was magnified by a microscopic objective, projected on a screen, and sketched upon a piece of paper. A tangent was drawn for the silhouette thus obtained, and the contact angle θ was measured using a protracter. pH of the solution was determined by the color indicator method before and after each treatment of the surface. As the solution had no buffer action, the experiment was

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(1) Reported before the annual meeting of the colloid chemistry held by the Chemical Society of Japan on Nov. 19th (1950).

(2) A. Inaba, This Bulletin, **23**, 146 (1950).

(3) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1406 (1937).

(4) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1762 (1937).

(5) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).

mainly conducted in the air free from carbon dioxide in the case of $pH > 6$. The use of a buffer solution was avoided owing to the probable effect of polyvalent anions and concentrated alkali ions which might obscure the effect of cation under investigation.

Results

The wettability of stearic acid surface treated by water, pH of which was controlled simply by hydrochloric acid or sodium hydroxide, is shown as a control curve in Fig. 1. In this case, wettability was constant in the range of $pH < 8$, being equal to that of untreated stearic acid towards distilled water ($\theta = 110°$), while the increase of wettability was remarkable at $pH > 10$, θ being reduced to almost 0°.

Addition of various metallic ions to the dipping solution affected the wettability of the stearic acid surface. These effects were divided into three types as follows:

(1) The Effect Produced by the Addition of Sodium, Potassium and Rubidium Salts.—The addition of these salts in concentration of 10^{-4} mol showed no effect on the wettability of stearic acid compared with the control as shown in Fig. 1. However, the increase of the concentration of the salts lowered pH at which wettability began to increase. For example, the addition of 0.05 mol Na_2HPO_4 or 0.2 mol KCl caused the wettability of stearic acid already at pH 7 (Fig. 1) to increase.

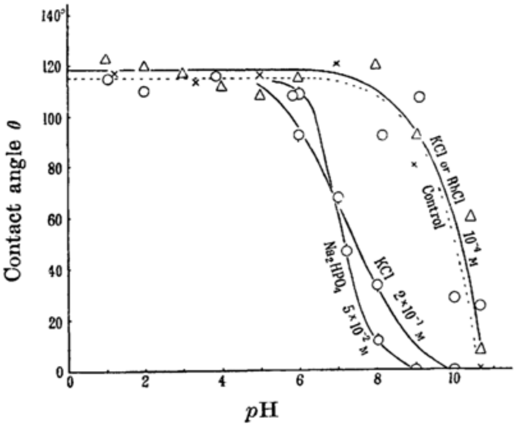

Fig. 1.—The effects of Na, K, and Rb ions (the 1st group) upon the wettability of stearic acid surface.

(2) The Effect Produced by the Addition of Thorium, Aluminum, Ferric, Chromic, Cobaltous and Cupric Salts.—These salts enhanced the wettability of the stearic acid surface in the pH region characteristic for each salt (Fig. 2a), although stearic acid showed only a small wettability in the absence of these salts (control curve). Cadmium, zinc, silver, and magnesium salts showed no effect at concentration of 10^{-4} mol but showed a perceptible wetting power at concentration of 10^{-3} mol (Fig. 2b). These salts may also be considered to belong to the preceding class, but for the reason mentioned later we should like to classify them as belonging to this class.

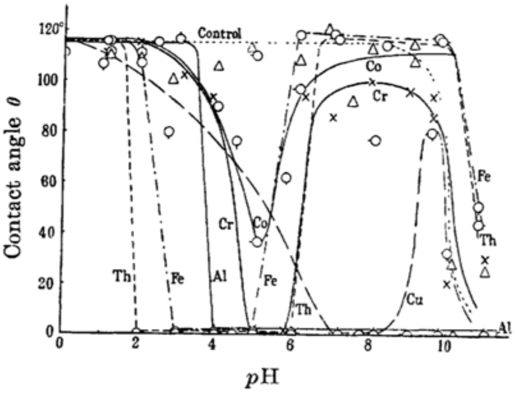

Fig. 2a.—The effects of Th, Fe, Al, Cr, Co, and Cu ions (the 2nd group) in concentration of 10^{-4} mol upon the wettability of stearic acid surface.

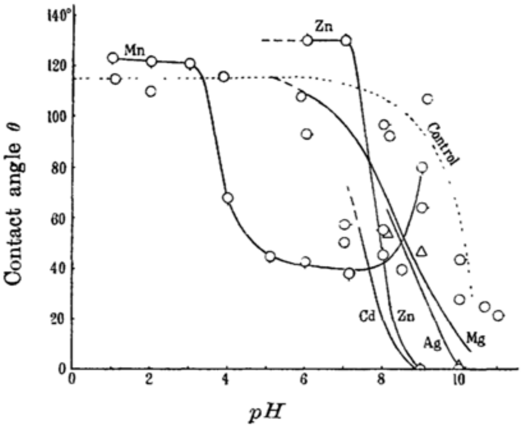

Fig. 2b.—The effects of Mn, Cd, Zn, Ag, and Mg ions (the 2nd group) in concentration of 10^{-3} mol upon the wettability of stearic acid surface.

(3) The Effect Produced by the Addition of Barium, Strontium, Calcium and Lithium Salts.—These salts reduced the wettability of stearic acid at $pH > 10$ (Fig. 3), in the region of which, however, stearic acid was wettable in the absence of these metallic ions except sodium ion which came from alkali for pH control. In this case increase in concentration of the ions of this group promoted the non-wetting properties of stearic acid as shown in Fig. 3. Mercuric, nickel, and lead salts showed apparently the similar effect (Fig. 4).

Discussion

Wettability of the stearic acid surface towards distilled water was small, the contact angle being

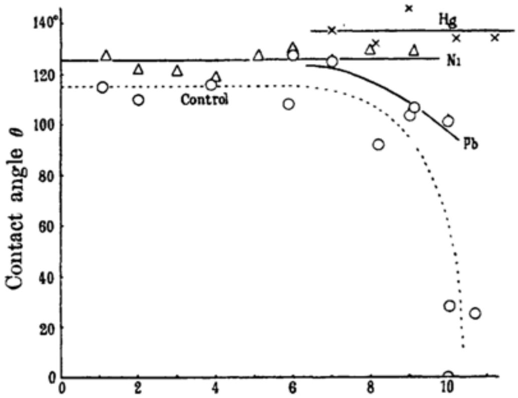

Fig. 3.—The effects of Ba, Sr, Ca, and Li ions (the 3rd group) upon the wettability of stearic acid surface.

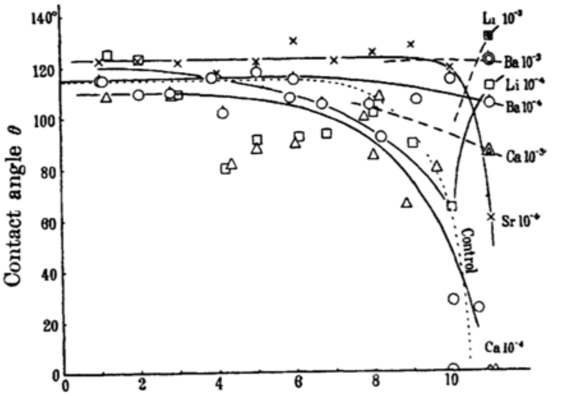

Fig. 4.—The effects of Hg, Ni, and Pb ions in concentration of 10^{-3} mol upon the wettability of stearic acid surface.

about 110°, and it did not change by being treated with hydrochloric acid. However, the surface showed increase in wettability towards sodium hydroxide solution. This increase can be explained by the polarity of the surface caused by the surface dissociation of stearic acid as follows:

$$\mathrm{StH+Na^{+}+OH^{-}=St^{-}Na^{+}+H_2O.}$$

This will explain the control curve of Fig. 1. A more detailed calculation can even predict the wettability ~ pH curve similar to that found experimentally as shown in Fig. 1. It may be presumed that the addition of neutral salt like KCl or $\mathrm{Na_2HPO_4}$ promotes the dissociation and that as a result wettability is increased. In fact, the wettability began to increase already at pH 7 as shown in Fig. 1.

Now we come to place where we can explain the effect of various metallic ions on the wettability of stearic acid. There have been some informations available for this purpose. For instance, we can cite Langmuir's study⁽⁵⁾ on the stearic acid monolayer on the substrate containing metallic ions. There he confirmed the adsorption of metallic ions to the monolayer. Especially, in the case of barium salt, stearic acid monolayer was considered to be composed of neutral barium soap at pH 11,⁽⁶⁾ and its built-up film was not wetted with water.⁽³⁾ The author's experiment showed that the surface of stearic acid treated with 10^{-4} mol cupric salt solution at pH 6 ~ 8 was bright blue and the color was not removed after rinsing with water. From these and also other similar phenomena encountered we can safely conclude the adsorption or chemical reaction taking place between stearic acid and the metallic ions in solution, which profoundly affect the wetting condition of stearic acid surface. We can also confirm this point more precisely. Langmuir and others⁽⁵⁾ introduced the following equation for this adsorption.

$$\log\{\gamma_1/(1-\gamma_1)\}=C_1+m_1\log[M_1{}^{Z+}]+Zm_1\,(p\mathrm{H})$$

Here γ_1 is the fraction of the number of surface cells occupied by the adsorbed substance, C_1 and m_1 are constants proper to $M_1{}^{Z+}$ ion. According to this equation, it can be expected that apart from the characteristic properties of ions, higher valency ions can be adsorbed at still lower pH than that at which the lower valency ions are adsorbed. Langmuir's results showed that ferric ions were strongly adsorbed by stearic acid monolayer at pH 2, and aluminum ions at pH 3 to 5, barium at pH 6, and sodium at pH 8. On the other hand, in the author's experiment the various effects of the ions upon wettability appeared in the pH regions shown in Table 1, which were based upon the data of Figs. 2a, 2b, 3 and 4. It can be noted that these pH regions for various cations as a whole are in close relationship with those given for cations by Langmuir in the case of adsorption. The fact again confirms the above view, that the adsorption of ions is an important factor affecting the wettability of stearic acid. Disappearence of the remarkable wetting

Table 1

pH Regions at which Metallic Ions Affect the Wettability of Stearic Acid Surface.

Ion	pH	Ion	pH	Ion	pH	Ion	pH
$\mathrm{Th^{++++}}$	2~6	$\mathrm{Fe^{+++}}$	3~5	$\mathrm{Co^{++}}$	5	$\mathrm{Li^{+}}$	>10
		$\mathrm{Al^{+++}}$	>4	$\mathrm{Cu^{++}}$	7~8		
		$\mathrm{Cr^{+++}}$	5~6	$\mathrm{Mn^{++}}$	5~8 (10^{-3} mol)		
				$\mathrm{Zn^{++}}$	>9 (10^{-3} mol)		
				$\mathrm{Cd^{++}}$	>9 (10^{-4} mol)		
				$\mathrm{Ba^{++}}$*	>10		

* $\mathrm{Ba^{++}}$ is considered to be partially adsorbed already at pH 6 or 7, but we cannot distinguish this surface from that of stearic acid at this pH, for both surfaces are non-dissociating and behave similarly at this pH.

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(6) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936).

Table 2

Relation between Wetting Power and Co-ordination Tendency of Metallic Ions

Ion	Type of wetting	Degree of wetting*	Ionic potential	Ionization potential (1st), e. v.	Normal electrode potential, volt	Heat of hydration, kcal./mole	Free energy decrease of complex formation with stearate radical
Na^+	1st class	0	1.02	5.12	−2.71	114	—
K^+	〃	0	0.75	4.32	−2.92	94	—
Rb^+	〃	0	0.67	—	−2.92	—	—
Li^+	3rd class	−	1.28	5.37	−2.96	136	1.3
Ca^{++}	〃	−	1.89	6.09	−2.81	410	1.2
Sr^{++}	〃	−−	1.57	5.67	—	376	—
Ba^{++}	〃	−−	1.40	5.19	—	346	(1.1)
Ni^{++}	(3rd class)	−	2.56	7.61	−0.234	516	2.5
Hg^{++}	(〃)	−	1.79	10.38	+0.85	480	6.1
Pb^{++}	(〃)	−	1.52	7.38	−0.13	—	(3.4)
Mg^{++}	2nd class	+	2.56	7.61	−1.87	490	1.4
Cd^{++}	〃	+	1.94	8.96	−0.40	462	2.7
Zn^{++}	〃	+	2.41	9.36	−0.76	528	2.9
Mn^{++}	〃	+	2.20	7.41	−1.03	479	—
Ag^+	〃	+	0.88	7.54	+0.80	162	3.5
Co^{++}	〃	++	2.44	8.5	−0.26	504	2.2
Cu^{++}	〃	++	1.98	7.68	+0.35	536	3.4
Cr^{+++}	〃	++	4.69	6.74	−0.51	—	(4.3)
Fe^{+++}	〃	++	4.48	7.83	−0.04	185	(3.6)
Al^{+++}	〃	+++	5.26	5.96	−1.69	1149	(9.7)
Th^{++++}	〃	+++	3.64	—	—	—	—

* 0: Degree of wetting power exhibited under control condition.
−, −−: Relative degree of non-wetting power perceptible at 10^{-3} mol and 10^{-4} mol respectively.
+, ++: Relative degree of wetting power perceptible at 10^{-3} mol and 10^{-4} mol respectively.
+++: Remarkable wetting power exhibited at 10^{-4} mol.

power of ferric, thorium, chromic, cobaltous, and cupric, ions in high *p*H region can be attributed to the decrease of concentration of these ions in solution due to the precipitation as hydroxide.

Now, we feel much interest in the question, "What is the chief factor determining the wetting or non-wetting power of an ion?" To answer this question, we must know the nature of these adsorption products of metallic ions on stearic acid, which may presumably be attributed to the structural characteristics of the metallic ions themselves. In this connection, it is best to pay attention to the co-ordination tendency of the individual metallic ion concerned.

First of all, let us consider the aluminum ion which showed remarkable wetting power. It was known to have a marked co-ordination tendency and to form an aquo ion, $Al(H_2O)_6{}^{+++}$, in water, which was considered further to form so-called ol-compound and oxo-compound through hydrolysis and association of more than two aquo ions.(7) On the other hand, many fatty acid-aluminum compounds were considered by many investigators(8) to be hydrated macro-molecules. Sasaki and Matuura of our laboratory also confirmed the fact that stearic acid monolayer on the aqueous substrate containing aluminum ions showed a remarkable expansion and rigidity, while the monolayer on a substrate containing barium or calcium ions had no such properties.(9) Muramatsu and Sasaki observed that the thickness of the built-up film of stearic acid conditioned with aluminum salt solution, was remarkably increased compared with that without conditioning.(10) All these results lead us to the conclusion that the adsorption product or chemical compound between aluminum and stearic acid is composed of relatively large molecules of a complicated structure, which are also suitable for the explanation of the wetting power of aluminum ion. The complexity of the adsorption product may of course come from the marked co-ordination tendency exhibited by aluminum ion. From this point of view we may postulate further, that a marked co-ordination tendency of any metallic ion towards both water molecule and stearate

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(7) N. Bjerrum, *Z. physik. Chem.*, A **59**, 336, 581 (1907), **73**, 724 (1910), **110**, 656 (1924).

(8) V. R. Gray and A. E. Alexander, *J. Phys. & Colloid Chem.*, **53**, 26 (1949); E. Eigenberger and A. Eigenberger-Bittner, *Kolloid-Z.*, **91**, 287 (1940); Hi. Ikeda, K. Shiroyanagi and Ha. Ikeda, *Reports of The Scientific Research Institute*, **25**, 353 (1949); I. S. McRoberts and J. H. Schulman; *Proc. Roy. Soc.* (London), A **200**, 136 (1950).

(9) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951). R. Matuura, This Bulletin **24**, 278 (1951)

(10) M. Muramatsu and T. Sasaki, This Bulletin, **25**, 21, 25 (1952).

radical favors the wettability of the treated surface. To ascertain this presumption, we examined the parallelism required to exist between the co-ordination tendency of metallic ion and wettability of stearic acid treated with the solution containing the same ions.

As the measure of co-ordination tendency or something closely related to this, the following factors are selected as shown in Table 2, namely free energy decrease of complex formation in aqueous solution, ionic potential,(11) ionization potential (1st ionization),(12) normal electrode potential,(13) and heat of hydration.(14) The value of free energy decrease of complex formation, $N/Z \cdot \log k + \log 55$ (Z, the co-ordination number of metallic ion, N, the number of ligands coordinated to central metallic ion,

$$\log k = \frac{1}{N} \log \frac{[MA_N]}{[M_{aq}]\,[A]^N}, \quad [MA_N], [M_{aq}] \text{ and } [A]$$

being the concentration of the complex, hydrated cation, and ligand respectively), which is proposed by Bjerrum,(15) is calculated for the case of stearate radical as ligand using the data for other ligand. As a whole, these five series are parallel to the series of the wetting power of metallic ions mentioned above (Table 2), though there are minor irregularities not completely explained yet. Among these the series of Bjerrum's free energy shows a good parallelism. In this case, it must be kept in mind that Bjerrum calculated the value for the complete exchange of aquo-molecule for other ligands, whereas in our case, we rather require the value for the exchange of the certain fraction of exchangeable aquo-molecule for stearate radical. The latter quantity may, however, be considered to be roughly parallel to the former.

Now, we should like to consider that cadmium, silver, and zinc ions belong to the second class because they have a rather large co-ordination tendency as can be expected from Table 2. The results of Muramatsu, Matuura and Sasaki(9)(10) also confirm this view. It can be noted however that nickel, mercuric and lead ions, in spite of their marked co-ordination tendency for stearate and of rather large heat of hydration, not only showed no effect of promoting the wettability of stearic acid but also exhibited a further reduction, when compared with the case of untreated stearic acid. These facts together with those obtained by Sasaki and Matuura lead us to postulate that these three ions might form another group. The author will refer to this point in a paper which will follow. Apart from these exceptions, the effect of the second group ions is considered to come from the macro-molecular structure of their adsorption product formed on stearic acid surface as mentioned already.

Sonders and others(16) insisted that the polarizability of metallic ions played an important role in the wettability when they were adsorbed on the surface of glass or clay. But their idea does not explain the wetting phenomena observed in the author's experiment.

It is required further to explain the effect of reducing the wettability due to the third group ions such as barium or calcium. Here, contrary to the macro-molecular structure of aluminum soap, barium soap is known to be a simple compound composed of the linkage of principal valency only, similarly as in the case of stearic acid. Therefore, the surface of barium soap is probably non-wettable as in the case of stearic acid in the region of low pH. The non-wetting power of barium stearate at $p\text{H}>10$, being different from the wettable property of stearic acid, is explained by the consideration that barium-soap is more stable against surface dissociation than free stearic acid in alkaline region. The stability is probably caused by a stronger binding force of stearate radical to barium than to hydrogen.

Thus, the wetting or non-wetting effect of the ions towards the stearic acid surface is briefly explained by either macro or simple molecular structure of the adsorption product. For the support of this view, it is worth while to point out further the following facts. It is generally recognized that the wettability is profoundly affected by the orientation or overturning of the surface molecules.(3) According to this view, together with our opinion concerning wettability, it may be expected that aluminum salt treatment renders the surface layer of stearic acid more difficult to overturn than in the case of barium salt treatment. Certainly, an easiness of overturning contributes to some extent to the non-wetting properties of a surface treated by barium salt. Thus the overturn theory not only does not contradict the experimental results and the opinion mentioned above, but also supports the result of measurements on wettability of stearic acid built-up film, which was already reported briefly by Muramatsu and Sasaki,(10) and will be described by the present author in detail in a paper which will follow.

Summary

The effect of the solution of various metallic ions at varying pH upon the wettability of stearic acid surface has been studied. These ions are adsorbed by stearic acid surface in characteristic pH region and are classified into the following three groups, according to their effects on wettability.

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(11) The values were calculated from those of ionic radii from W. L. Bragg, "Atomic Structure of Minerals", Cornel University Press, New York (1937).

(12) R. F. Bacher and S. Gaoudsmit, "Atomic Energy States" McGraw-Hill Book Co., Inc., New York and London (1932).

(13) M. de K. Thompson, "Theoretical and Applied Electrochemistry" The Macmillan Co., New York (1939).

(14) J. D. Bernal and R. H. Fowler, *J. Phys. Chem.*, **1**, 515 (1933).

(15) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950)

(16) L. R. Sonders, D. P. Enright and W. A. Weyl, *J. Applied Phys.*, **21**, 338 (1950).

(1) Wetting ions 1	Formation of ionic adsoption compound (surface dissociation).	Na, K, and Rb.
(2) Wetting ions 2	Formation of hydrated, macromolecular adsorption compound.	Al, Th, Fe, Cr, Co, Cu, Zn, Cd, Mn and Ag.
(3) Non-wetting ions	Formation of simple molecular non-dissociating compound of mere principal valency.	Ba, Sr, Ca, and Li.

The classification has been based upon the structural characteristics of the ions, especially the co-ordination tendency of the ions. The theory of overturning of molecules in surface layer is also one of the probable supports of these opinions.

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